BORON TRIFLUORIDE CATALYSIS OF PHOTODIMERIZATION OF COUMARINS AND PSORALENS AND THEIR CROSS CYCLOADDITION TO TETRAMETHYLETHYLENE

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Résumé : Nous étudions les effets de la complexation par BF₃ sur les réactions de photodimérisation et de photocycloaddition, avec le 2,3-diméthylbut-2-ène, de la coumarine 1, des 7-méthoxy et 5,7-diméthoxycoumarines 2 et 3 et des 5- et 8-méthoxypsoralènes 4 et 5. L'observation de points isobestiques dans les spectres électroniques et de modifications des spectres IR en présence de BF₃ indiquent la formation d'un complexe entre l'acide de Lewis et l'oxygène du groupement carbonyle du cycle pyrone. La formation d'un exciplexe singulet conduit à une augmentation du rendement et de la stéréosélectivité de la réaction. BF₃ se comporte comme un catalyseur pour les réactions impliquant le passage par un état singulet et comme un inhibiteur pour celles impliquant un état triplet.

*Mots clés : Coumarines, Psoralènes, Photodimérisation, Photocycloaddition,
Acide de Lewis.*

I - INTRODUCTION

The photoreaction of coumarins and psoralens has been extensively investigated, notably the dimerisation and cycloaddition using alkenes, DNA and its pyrimidine bases. The furocoumarins compounds are

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able to intercalate inside DNA, and by subsequent irradiation with UVA light, to photoreact with DNA. The photoreaction already known, consists of a (2+2) cycloaddition reaction with the pyrimidine bases [1]. However, results are often scanty and rarely comparable because of differences in experimental conditions. Nevertheless, it is well known that photochemical processes are complex, and parameters such as : concentration, temperature, physical status, type of solvent, etc. can significantly influence photochemical reaction processes.

Furthermore, the 7-methoxycoumarin 2 and the 5, 7-dimethoxy-coumarin 3 (scheme 1) were extensively studied under various conditions. The study of these two compounds were systematically reconsidered mainly with regard to dimerisation and photocycloaddition processes with tetramethylethylene (TME) under similar experimental conditions, in order to monitor their photochemical behaviour.

In the past, only the substituted furocoumarin, 8-methoxypsoralen 5 was the compound used in phototherapy of a number of skin diseases such as psoriasis and vitiligo[2,3]. Numerous studies were conducted on the photochemical behaviour of this compound under different experimental conditions in order to get a better understanding of its photo biological and photo medical properties. However in the past two decades, the negative mutagenic effect of this compound responsible for skin cancer was observed. For this reason, physicians and biologists are now trying to turn to other more efficient and less toxic compounds. The 5-methoxypsoralen, compound 4 has been used for the past decade as an efficient drug in the treatment of psoriasis. This drug tends to replace 8-methoxypsoralen 5. Despite genotoxic properties, it causes less adverse effects and is well tolerated by patients.

This compound has received little attention and as a result, its photochemical properties are not well known. This led us to consider that a study of these two compounds in similar experimental conditions is a necessity.

Photoreactivity studies of the two furocoumarins *vis-à-vis* the dimerisation and the addition processes of an alkene (TME) were undertaken under conditions similar to those used previously. The aim was to compare the two molecules and to try to show the influence of the furan nucleus on the coumarins.

Photosensibilisation and quenching play a significant role in photochemistry. The ability of Lewis acids to serve as a catalyst for photochemical reactions has been recognized for many years [4]. In particular Lewis acids serve as catalysts for photochemical (2+2) cycloaddition reaction such as photodimerization[4d-5]. Shim[5a] has also studied the influence of Lewis acids on the photoreactivity of 5,7-dimethoxycoumarin. We found it necessary to repeat previous experiments in the presence of BF_3OEt_2 in order to analyse the effects of BF_3 on reactional processes. So, we investigated spectroscopic properties, photodimerization and cross photocycloaddition with tetramethylethylene (TME), of coumarin **1**, the two methoxycoumarins, **2**, **3** and methoxypsoralens **4**, **5** (Scheme 1), in the presence and the absence of boron trifluoride etherate as Lewis Acid.

1 : $R_1 = R_2 = H$ 4 : $R_1 = OCH_3$; $R_2 = H$
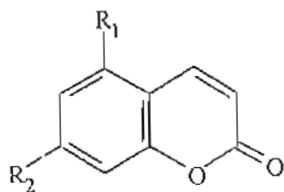
2 : $R_1 = H$; $R_2 = OCH_3$ 5 : $R_1 = H$; $R_2 = OCH_3$
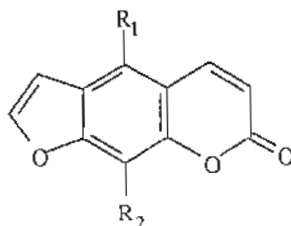
3 : $R_1 = R_2 = OCH_3$

EXPERIMENTAL

Materials

Coumarins, psoralens, 2,3-dimethyl but-2-ene and boron trifluoride etherate were purchased from Aldrich and used as received except for 5,7-dimethoxycoumarin which was sublimated before use. Dichloro methane was treated with a 5% solution of sodium carbonate, dried over calcium chloride and distilled before use. Other solvents (pure grade) were used without further purification.

General Methods

Ultraviolet absorption spectra were obtained on a Beckman Model 25 spectrometer. Solid state infrared spectra were recorded on a 7199 Nicolet FT-IR spectrometer with 2 cm^{-1} resolution using KBr pellets. ^{1}H NMR spectra were measured in CDCl$_3$ or in DMSO-D6 using a Varian EM 360 (60 MHz) or a Brucker 200 Spectrometer (200 MHz), or a Brucker AM 400 Spectrometer (400 MHz). The chemical shifts, are relative to tetramethylsilane and expressed in parts per million (ppm), the coupling constants are in hertz.

Irradiation Procedures

The samples were irradiated 45 cm from the light source, with 450 W high pressure mercury lamp ($230 < \lambda < 900$ nm) equipped with a quartz envelope. The glass reaction cells filtered the beam at $\lambda > 310$ nm. Reactions were monitored by UV-visible spectrometry. After irradiation the samples were concentrated by rotatory evaporation under reduced pressure. The crude photoproducts were analysed by ^{1}H NMR and IR before purification. Photoproducts were isolated by fractionnal crystallization and the purities controlled by ^{1}H NMR spectroscopy at 400 MHz.

Irradiation in Presence of BF$_3$ OEt$_2$ - General Procedure

Compounds were dissolved in 50 ml of dichloromethane in a pyrex

flask and the degassed solution with N_2, BF_3OEt_2 was added to the sample with a syringe and the flask seales under vacuum. The sample was then irradiated for many hours, table I.

Compounds	Uncatalyzed Experiments				Catalyzed Experiments				
	Concentration M1 (solvant)	Irradiation time hours	Global yields %	Photoisomers (%)	Concentration M1 (CH2Cl2)	BF3OEt2 equivalent molar	Irradiation time hours	Global yields %	Photoisomers (%)
1*	0.1 (CH3Cl)	-	-	-	0.02*	-	36	96	cis-anti (100) / trans-syn (94) [g]
1'	0.56 (EtOH)	72	10	cis-syn (96) / trans-syn (4)	0.02*	-	72	85	cis-anti (100)
2'	0.05 (CH2Cl2)	-	-	trans-syn (14) / cis-syn (86)		0.5	65	54	cis-anti (100)
2	0.05 (CH2Cl2)	45	65	cis-syn (65) / cis-anti (23) / cis-anti (12)	0.05*	0.25	65	66	cis-anti (100)
2*	0.1 (CH3CN)	-	-			0.16	45	61	cis-anti (100) / trans-syn (94) [g]
3*	0.1 (CH3CN)	15	-	trans-syn (100)	0.05*	0.03			cis-anti > trans
3'	0.05	30	-	trans (100)					
4	0.05 (CH2Cl2)	60	50	cis-anti (85)	0.05*	0.03	40	40	trans-syn (15) / cis-anti (85)
4*	0.02 (CH3CN)	6	100	trans-syn (18) / trans-anti (80)	0.02*	0.03	6	10	cis-anti (85)
5'	0.05 (CH3Cl2)	-	-	trans-anti (100)		0.03	45	13	trans-syn (100)
5*	0.05 (CH3Cl2)	45 / 22	-	trans-syn [10]	0.05*	0.25	45	5	trans-syn (100)

TABLE I : Products comosition for dimerizition experiments. a: This work ; b : see ref. 14 ; c : see ref. 4d ; d : sensitized photolysis ref 6b ; e : see ref. 5a f : see ref. 8d. and 9, the same esult is obtained in sensitized expriment ; g : see ref. 16

Irradiation with TME in Presence of BF_3OEt_2 -General Procedure

Compounds and BF_3OEt_2 were combined with dichloromethane in the pyrex cell and allowed to stand for approximately 15 minutes. Tetramethyl ethylene (1.18 ml, 10^{-2} mol) was then added to the flask and the solution diluted to 50 ml with additional dichloromethane. The cell was degassed, sealed and irradiated with 450 W lamp for 4h, Table II.

TABLE II : *Yield of Cross photocycloaddition reactions. a: This work, In any experiments we have a large excess of TME, Irradition time is 4 hou rs ; b : see ref. 14 ; c : see ref. 4d ; d : we obtain also 5% of cis -anti photodimer ; e : see ref. 6a f : see ref. 6d.*

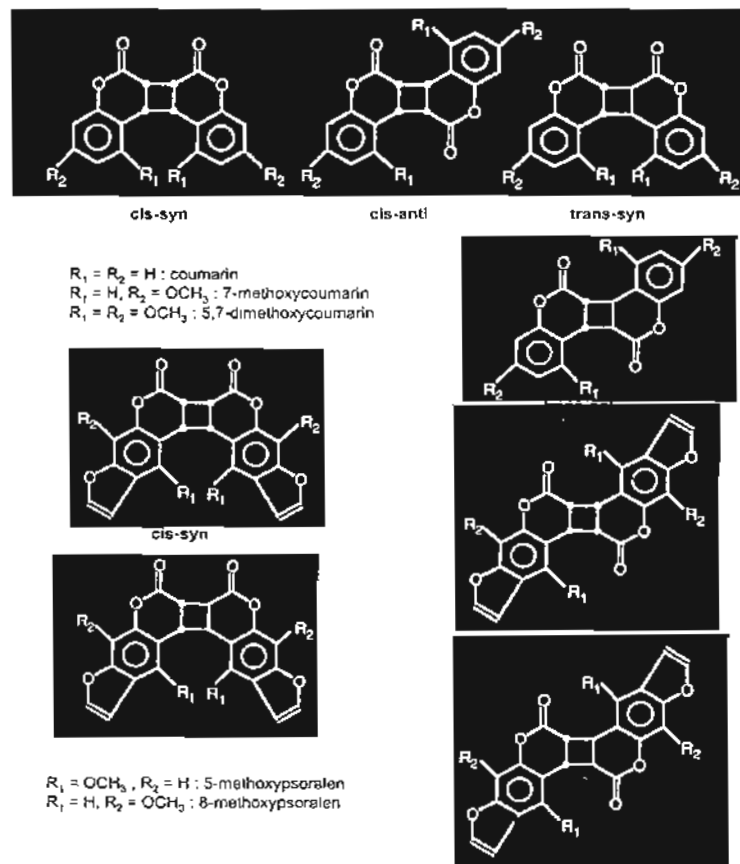| | Uncatalysed Experiments | | Catalysed Experiments | BF$_3$OEt$_2$ | |
Compounds	Concentration M l^{-1}	Yields %	Concentration M l^{-1}	equivalent molar	Yields %
1	0.1	4[b]	0.02	0.5	57[c]
2[a]	0.02	28[d]	0.02	0.25	41
2[a]			0.02	0.50	49
2[a]			0.02	3	52
3[e]	0.005	not given			
3[e]	0.02	100	0.02	0.03	93
3[e]			0.02	0.25	63
4[a]	0.02	100	0.02	0.25	63
5[f]	0.002	not given			
5[a]	0.02	28	0.02	0.03	22
5[a]			0.02	0.25	12

RESULTS AND DISCUSSION

Table I shows experimental results for uncatalyzed and boron trifluoride catalyzed dimerization. In table II experimental results for uncatalyzed and catalyzed photocycloaddition with TME are reported. Our results are compared with those previously obtained by Lewis [4d] and Shim [5a, 6] for coumarin 1,5,7-dimethoxycoumarin 3 and 8-methoxypsoralen 4. To eliminate the influence of solvent on the product ratio [7] and to provide a basis for comparison of Lewis acid catalyzed versus uncatalyzed reactions, we have carried out the experiments in dichloromethane solutions. The different photoproducts in the crude solid obtained after evaporation of the solvent of the irradiated samples, were purified by fractionnal crystallization. Their purities were controlled by ^{1}H NMR spectroscopy at 400 MHz.

In our experiments with 5- and 8-methoxypsoralens the (2+2) cycloaddition occurs exclusively at the C_3-C_4 double bond of the pyrone ring, as observed previously[8-11]. In contrast, the photoreaction of psoralens derivatives and other analogue compounds with the thymidine bases of DNA, proceeds with cross-linking in both the double bond sites of the furan C_4-C_5, and the pyrone C_3-C_4 rings. The furan double bond is the more reactive, but this fact is some times debated [1,9,12].

The structures of the photodimers (Scheme 2) were established by comparison of their ^{1}H NMR and IR spectra with those described in the litterature for similar products[8-10] (Table III). Four photodimers can be expected with a cis-syn, cis-anti, trans-syn or trans-anti organization around the cyclobutane ring resulting from the (2+2) cycloaddition (scheme 2).

65

cis-syn   cis-anti   trans-syn

R$_1$ = R$_2$ = H : coumarin
R$_1$ = H, R$_2$ = OCH$_3$: 7-methoxycoumarin
R$_1$ = R$_2$ = OCH$_3$: 5,7-dimethoxycoumarin

cis-syn

R$_1$ = OCH$_3$, R$_2$ = H : 5-methoxypsoralen
R$_1$ = H, R$_2$ = OCH$_3$: 8-methoxypsoralen

Scheme 2

	coumarin 1	7-méthoxy- Coumarin 2	5,7-diméthoxy- Coumarin 3	5-méthoxy- Psoralen 4	8-méthoxy- Psoralen 5	Attribution
Monomer	3110	3088	3080	3180	3140	νC-H furan
			3050	3144	3113	νC-H furan
				3116	3118	νCH pyron
				3078	3098	
				3038		
	1714	1720	1711 VS	1734 VS	1718	νCH pyron / νC=O
	1706 VS	1706 VS	1709	1716	1706 VS	νC=O
	1594	1614	1611	1592	1585	νC=C pyron
				1542-1550	1547	νC=C luran
	828	850	820	821	821	=C-H Pyron
	C5 cis-syn	C5 cis-anti	cis-anti	trans-anti	trans-syn	
				3150	3150	νC-H luran
				3144	3140	
					3113	
Dimers	2981	2998		2900		γC-H cyclobutan
	2972	2988	2970	2968	2963	νC=C luran
	2960	2978	2961	2957	2848	
	2948	2947			2948	
		2989				
	1758 VS	1754 VS	1760 VS	1764 VS	1760 VS	νC=O
	1746	1750	1752	1752	1748	
	1374	1366	1353	1344	1345	Cycle vibrations
	1332	1334	1295	1321	1331	Coupled with C-H vibratione
	1280	1270	1255	1280	1232	
	1246	1246	1255	1244	1239	
	1190	1190	1185	1191	1193	
	1146	1143	1143	1145 (1137)	1134	
	1112	1106	1108	1110	1112	
	900	835	950	852	875	C-H cyclobutan

TABLE III : *Infrared spectra of monomers and dimers. VS : very strong. (The underlined vibrations are the strongest)*

Uncatalysed Reactions

From the results summarized in Tables I and II, we can observe that for the uncatalyzed reactions the yield is enhanced by a methoxy substituent, as previously observed [6b]. Likewise a methoxy group in position 5 of psoralen is more efficient than in position 8. As generally observed, Lewis [4d] showed that for coumarin 1, cis-syn and cis-anti cycloadduct compounds proceed from singlet excited state and trans-syn and trans-anti cycloadducts from triplet state. From fluorescence and phosphorescence experiments, Mantulin and Song[11] concluded to singlet excited state for 2 and 3 and triplet ones for hydroxy psoralens derivatives.

Now if we analyze the configurations of the dimers inTable I, we can observe that their structures are correlated with the nature of the excited state, for example, the cis-syn and cis-anti dimers are the majors photoproducts for coumarins 2 and 3. From these results we can conclude that uncatalyzed dimerization proceed from singlet and triplet states for 1, 2, 3 and exclusively from triplet states for 4 and 5.

For uncatalyzed reaction of compounds 1, 2, 3, 4 and 5 with TME we obtain only cycloaddition on the pyrone ring (scheme 3, table IV). Our results are in agreement with thoses of Bethe and al[13] who have studied the photocycloaddition of furocoumarins derivatives with TME, and obtained a cyclobutane monoadduct with this olefin at the pyrone C_3-C_4 double bond side. This data also fully correlate with those of the cycloadducts of coumarins to the same alkene[14] and to thymine[15].
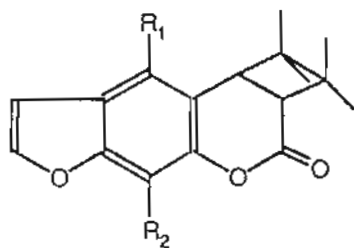
SCHEME 3 : *Structures of the photoadducts of the TME*

1a : $R_1 = R_2 = H$ 4a : $R_1 = OCH_3$; $R_2 = H$
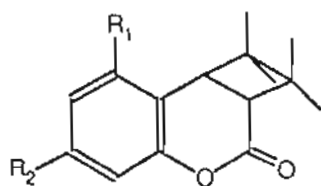
2a : $R_1 = H$; $R_2 = OCH_3$ 5a : $R_1 = H$; $R_2 = OCH_3$

3a : $R_1 = R_2 = OCH_3$

<u>TABLE IV</u> : *Spectroscopic data of photoadducts with TME.*
   a)   KBr pellets, n in cm⁻¹, b) d in ppm from TMS, m massif, s singlet ,
   d doublet, dd doublet of doublet, solvent CDCl₃

|	$\nu\,C = O^a$	$^1H\,NMR^b$
1	1745	0.75 (3H,s), 1.02 (3H,s); 1.22 (3H,s); 1.27 (3H,s); 3.18 (1H,d,J=10); 3.38 (1H,d,J=10); 7.10 (4H,m)
2	1735	0.72 (3H,s) ; 1.02 (3H,s) ; 1.20 (3H,s) ; 1.20 (3H,s) ; 1.27 (3H,s) ; 3.13 (1H,d,J=10) ; 3.35 (1H,d,J=10) ; 6.57 (1H,d,J=2) ; 6.65 (1H,dd,J=8.2) ; 6.92 (1H,d,J=2)
3	1755	0.72 (3H,s) ; 1.03 (3H,s) ; 1.18 (3H,s) ; 1.28 (3H,s) ; 3.07 (1H,d,J=10) ; 3.47 (1H,d,J=10) ; 3.82 (6H,s) ; 6.17 (2H,s)
4	1750	0.72 (3H,s) ; 1.03 (3H,s) ; 1.22 (3H,s) ; 1.31 (3H,s) ; 3.12 (1H,d,J=10) ; 3.72 (1H,s) ; 4.2 (3H,s) ; 6.77 (1H,s) ; 7.13 (1H,d,J=2.6) ; 7.7 (1H,d,J=2.6)
5	1744	0.73 (3H,s) ; 1.03 (3H,s) ; 1.20 (3H,s) ; 1.30 (3H,s) ; 3.13 (1H,d,J=10) ; 3.51 (1H,d,J=10) ; 4.16 (3H,s) ; 6.63 (1H,d,J=2.4) ; 6.8 (1H,s) ; 7.53 (1H,d,J=2.4)

Catalyzed Reactions

Before any comparison between the uncatalyzed and catalyzed reactions, it was necessary to know for each compound the effects of BF_3OEt_2 on the photodimerization and on the photocycloaddition.

### *Complexation by BF_3OEt_2*

The shift of the $vC=O$ streching vibration to lower frequency observed by infrared spectroscopy shows that the addition of Lewis acid to the compound in solution causes complexation on the carbonyl oxygen[4d,5].This fact is controlled by the evolution of the initial UV spectra of the compounds. For example addition of a small amount of BF_3OEt_2 to a solution of 4 leads to a reduction of the 308 nm absorption band and the appearance of a shoulder at $\lambda = 334$ nm. For this compound, we observe (Figure Ia), an isobestic point at $\lambda = 322.5$ nm indicative of this complexation. A similar result was obtained for 7-methoxy coumarin 2 : diminution of the 320 nm absorption band, apparition of a new absorption at $\lambda = 350$ nm with existence of an isobestic point at $\lambda = 333$ nm (Figure Ib).

FIGURE IA : *Absorption of 4.2 10⁻⁵ mol. l⁻¹ solution of 4 In the absence of*
BF₃OEt₂ (a), in the presence of 1.6 10⁻³ mol. l⁻¹ (b), 2.4 10⁻³ mol. l⁻¹ (c) and 6.5
10⁻³ mol. l⁻¹ (d) of BF₃OEt₂. The isobestic point is observed at λ = 322.5 nm.

Wave length (nm)
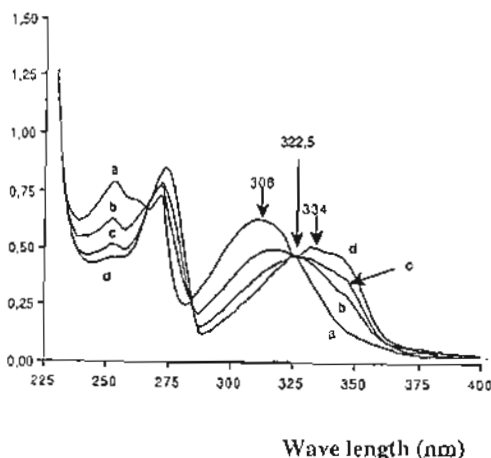
FIGURE IB : *Absorption of 9.05 10⁻⁵ mol. l⁻¹ solution of 2 in the absence*
of BF₃OEt₂ (1). In the presence of 4.54 10⁻³ mol. l⁻¹ (2), 7.95 10⁻³
mol. l⁻¹ (3) and 9.08 10⁻³ mol. l⁻¹ (4) of BF₃OEt₂. The isobestic point
is observed at λ = 333 nm.

Wave length (nm)

Optical density

72
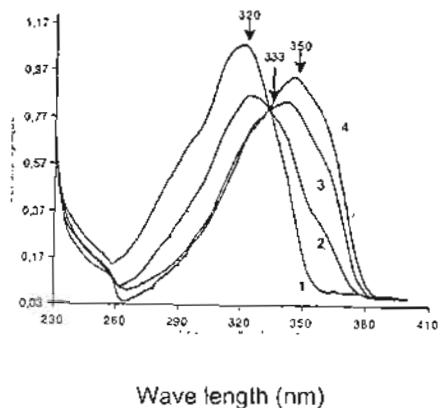
Effects on the Photoreactivity

In Figures II and III respectively are summarized the evolution of the yields for the dimerization and for the cross photocycloaddition of 2 and 5 with different concentrations of BF_3OEt_2. As observed for coumarin [5a] in the case of 2 (Figure IIa) the dimerization first increased and then decreased with BF_3OEt_2 concentration higher than 0.25 equivalent. Similar results were obtained for the cycloaddition reaction with TME (Figure IIb) but the maximum yield is obtained with higher concentrations (0.5 equivalent). In contrast for 8-methoxypsoralens 5, the yield of the two reactions decreases rapidly, as shown in figures IIIa and IIIb. In the case of 4 no dimer formation was observed in the presence of 0.25 equivalent of BF_3OEt_2 (Table I).This evolution is similar to those reported by Shim in the case of $3^{[5a]}$.

To compare catalyzed versus uncatalyzed reactions, each catalyzed experiment was carried out with the optimized BF_3OEt_2 concentrations as is reported in Tables I and II.Results of catalyzed reactions (Tables I and II) show a characteristic enhancement of the stereospecificity (only one photodimer observed) if we exclude compound 3^3. we observe two different behaviours for the photochemical reactivity. For compounds 1 and 2, the enhanced photochemical reactivity of complexed reactions may be interpreted as an increased singulet lifetime state. Therefore, For compounds 4 and 5, which involve triplet reaction pathway, through intersystem crossing, the decreasing photochemical reactivity in catalysed reactions is easily expected by quenching of the singlet state. For compounds 3 and 5, a plot of R_0/R versus $BF_3 OEt_2$, where R_0 and R are the reaction yield without and with quencher respectively, gives a straight line as predicted by Stern-Volmer quenching equations.The values of the slopes (117 and 262 $mol^{-1}l$) show that BF_3OEt_2 is a better quencher for psoralens than coumarins.

FIGURE II : *Yields for dimerization (a) and cross cycloaddition with TME (b)
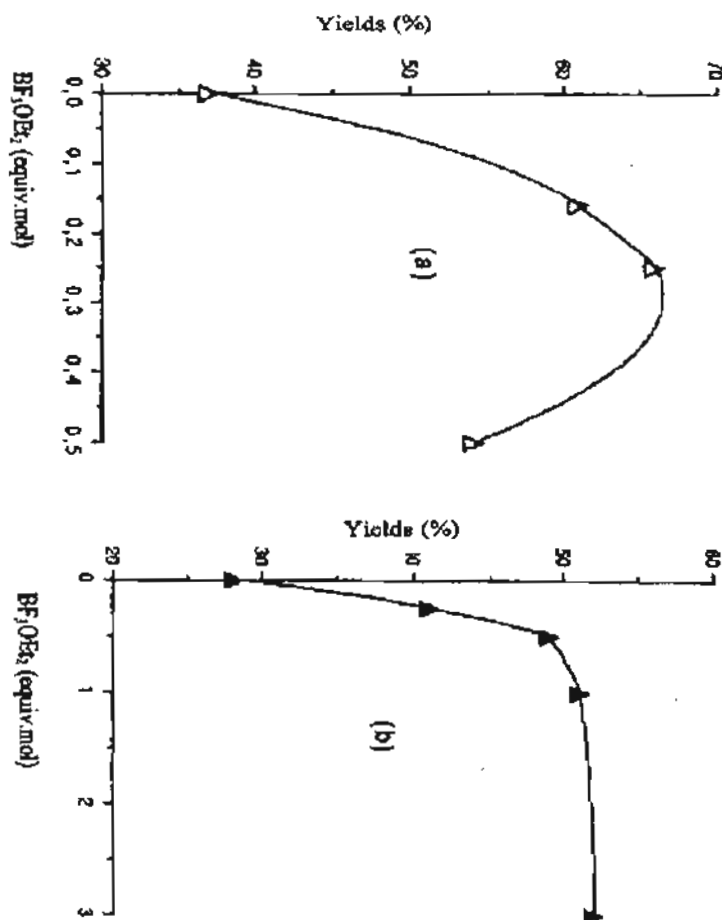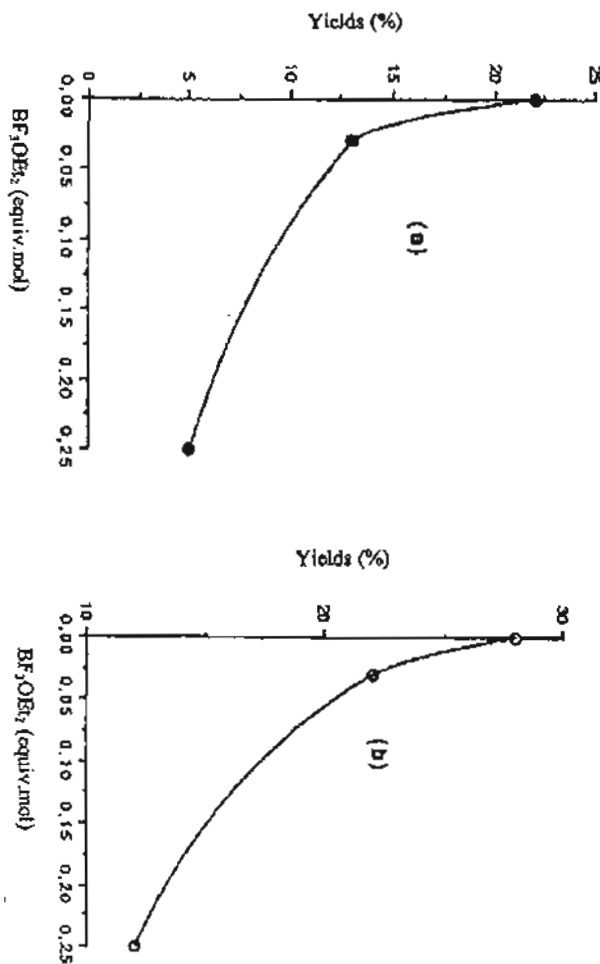of 2 (2.10^{-2} M) in the presence of BF$_3$OEt$_2$*

FIGURE III : *Yields for dimerization (a) and cross cycloaddition with TME (b) of 5 (2.10^{-2} M) in the presence of BF_3OEt_2*

CONCLUSION

To sum up, we have shown, as Lewis showed for coumarin[4d], that complexation of the pyrone carbonyl of methoxy coumarins or psoralens induces an exciplex formation under irradiation. Only the singlet exciplex undergoes a reaction with an enhancement of the photochemical reactivity and of the stereoselectivity. We conclude that BF_3OEt_2 is a catalyst for singlet excited state reactions and an inhibitor for triplet ones .

§ In ref. 6a and 6c Shim and coworkers showed by fluorescence quenching experiments that the photochemical reactivity of 3 is expected to be different from that of other coumarins.

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